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Polarized Raman study of phonon modes perturbed by the off-center Li^+ impurity in KCl

Wim Joosen, Etienne Goovaerts, and Dirk Schoemaker
Department of Physics, University of Antwerp (Universitaire Instelling Antwerpen), B-2610 Wilrijk, Belgium

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In KCl:Li^+ crystals a Raman-active resonance associated with the Li^+ off-center impurity was observed. The Raman signal is a broad line with a full width at half maximum of 15 cm^{-1} and is centered at 43 ± 2 cm^{-1}, which is almost coincident with the far-infrared transitions of this defect. The behavior-type method was applied to determine the symmetry and the irreducible representation of this Raman mode. It is found to belong to the A_{1g} representation of the cubic group O_h. This strongly indicates that a continuum of perturbed lattice modes is observed, and not the vibration in an off-center potential well of the Li^+ ion itself. The small and negative isotope shift upon $^7Li^+$ to $^6Li^+$ substitution also supports this idea. As such, the C_{3v} symmetry of the off-center Li^+ ion in KCl is not reflected in the polarized Raman intensities of the 43-cm^{-1} mode. However, the displacement from the on-center site softens the selection rules of scattering and absorption and this explains the approximate degeneracy of the Raman and ir transitions.

I. INTRODUCTION

The off-center position of the substitutional Li^+ ion in KCl is well documented. In Refs. 1 and 2, a review is given of the large amount of theoretical and experimental work that had been devoted to this system up until 1975. At an early stage of investigation of tunneling in solids, much effort was spent to determine the splittings of the tunneling states, which are 0.8 and 1.15 cm^{-1} for $^7Li^+$ and $^6Li^+$ in KCl, respectively. The properties of the ground-state multiplet of KCl:Li^+ are described by the tunneling model put forward by Gomez, Bowen, and Krumhansl (GBK).[3] It embeds the Li^+ ion in a static potential of cubic symmetry which possesses eight off-center minima along the $\langle 111 \rangle$ directions.

In 1970, Kirby *et al.*[4] reported a far-infrared dynamical mode of KCl:Li^+ at about 40 cm^{-1}, showing a negative isotope shift upon $^7Li^+$ to $^6Li^+$ substitution. They assumed a C_{3v} local symmetry and attributed this infrared (ir) mode to a motion of the Li^+ ion in an off-center potential well. Subsequently, the behavior of the ir mode under increasing hydrostatic pressure was studied.[5] So far, the ir transition and its behavior under hydrostatic pressure are not well understood, essentially because the GBK model (the tunneling approximation) is not adequate to describe the vibrational excited states.[4,5]

Recently, in the course of our Raman investigation of the hydrogen-tagged Li^+ center,[6,7] we observed a low-frequency Raman-active mode associated with the Li^+ defect and established[7] the nature of this mode based on a behavior-type analysis of the intensities of the polarized Raman data. Independently, Mabud and Lüty,[8,9] have detected this resonance, measured its polarized Raman spectra, observed a small and negative isotope shift similar to the one seen in the far ir, and reported on the nature of this Raman mode. In the present paper, we present the detailed analysis of our polarized Raman data based on the inductive behavior-type (BT) method,[10,11] and the approach of Kirby *et al.*[4] is reconsidered on the basis of the results of this analysis.

The outline of this paper is as follows. Experimental details are given in Sec. II. In Sec. III, the polarized Raman measurements of the dynamical mode are presented and the behavior-type (BT) method[10,11] is applied to determine the defect symmetry and the representation to which the resonant mode belongs. A key question is whether or not the C_{3v} $\langle 111 \rangle$ off-center symmetry will be observed. It will be shown that the Raman data point to a totally symmetric mode in a cubic defect symmetry.

In Sec. IV, the nature of the Raman and ir modes is discussed. A comparison with the Raman modes of the $F_A(Li^+)$ center in KCl is given. It is argued that the off-center Li^+ position is consistent with nearly degenerate Raman and ir transitions. Finally, we suggest a theoretical model to study the interaction between a continuum of perturbed lattice phonons, i.e., the resonant mode, and a tunneling system.

II. EXPERIMENTAL PROCEDURE

The Li^+-containing KCl samples were grown from a melt typically containing 2 mol % of LiCl with natural isotope abundances of 93% ^7Li and 7% ^6Li. The polarized Raman measurements were performed with 500-mW Ar^+ laser excitation at 514.5 nm on samples which were polished along the (110), $(1\bar{1}0)$, and (100) crystal planes. In order to suppress the elastic scattering by the polished plane, the Raman apparatus was used at a resolution of one wave number, which results in a relatively low throughput of the monochromator. Further details about the Raman equipment are given in Ref. 10.

III. POLARIZED RAMAN MEASUREMENTS AND BEHAVIOR-TYPE ANALYSIS

The BT method was developed to analyze polarized Raman data of defects in cubic crystals and to investigate systematically the defect symmetry and the representation to which a dynamical mode belongs. It is extensively discussed in Ref. 8, and we will refer to the tables of this paper in the course of the analysis presented in this section. Reference 9 can be recommended as a conceptual introduction to the BT method. The BT method has been successfully applied to several interstitial hydrogen atom defects in alkali halides[6,12] and to the resonant Raman spectra of the laser-active $Tl^{(0)}(1)$ center.[13] In these references, a detailed description of the application of the BT method to actual vibrational modes is presented.

The KCl:Li$^+$ system is representative of a whole class of defects exhibiting low-frequency Raman and/or ir-active resonances, and offers, as such, an entirely new type of dynamical mode to be studied by the BT method. Apart from this aspect, one may expect to observe spectral features, which are related to the tunneling motion of the Li$^+$ ion. However, it will be shown that the Raman resonance can offer only indirect information concerning the tunneling properties, through the small and anomalous isotope shift. The tunneling reorientation motion makes it impossible to produce a non-random-orientational distribution of Li$^+$ among its eight possible directions in the absence of an external field. Therefore, only the polarized Raman measurements on randomly oriented defects can be performed. The data are presented in Fig. 1.

From Fig. 1, the following relations are verified within experimental accuracy:

$$I_{x\bar{y},z}=s=0\ , \tag{1a}$$

$$I_{x\bar{y},x\bar{y}}=\tfrac{1}{2}(q+r)+s\neq 0\ , \tag{1b}$$

$$I_{xy,x\bar{y}}=\tfrac{1}{2}(q-r)=0\ . \tag{1c}$$

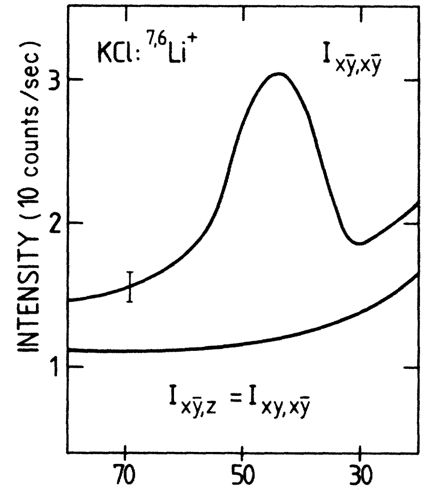

FIG. 1. Polarized Raman spectra of Li$^+$ in KCl, recorded at 10 K. The spectra have been smoothed for presentational purposes. The error bar is an estimate for the intensity fluctuations of the unsmoothed spectra.

$I_{\alpha,\beta}$ are the experimental polarized Raman intensities with α and β indicating the polarization of the incident and scattered light, respectively. q, r, and s are shorthand notations for the so-called intensity parameters (IP).[10,11] Within the experimental accuracy, one has the following typical IP relations:

$$q=r\neq 0\ , \tag{2a}$$

$$s=0\ . \tag{2b}$$

The relations (2) define BT 13 (Table VII of Ref. 10), which corresponds (Table VIII of Ref. 10) to an A mode of the tetrahedral symmetry T. This so-called representative mode represents five possible dynamical modes, namely (Table VI of Ref. 10)

$$T{:}A,\ \ T_h{:}A_g,\ \ O{:}A_1,\ \ T_d{:}A_1,\ \ O_h{:}A_{1g}\ .$$

At this point, the BT method cannot discriminate further, but its essential result is that *the observed Raman mode at 43 cm^{-1} belongs to a totally symmetric representation of a tetrahedral or a cubic symmetry.* For further discussion, we restrict ourselves to the A_{1g} mode of the full cubic group O_h, in agreement with the symmetry adopted in the GBK model. This Raman result may be called surprising: The Li$^+$ ion in KCl is a well-known $\langle 111\rangle$ off-center impurity and the frequency of the incident light (10^{15} Hz) is high enough to detect the Li$^+$ ion in an off-center localized pocket state, since the tunnel frequency is of the order of 10^{10} Hz.

IV. DISCUSSION

A. Nature of the Raman and ir resonances of the Li$^+$ center

First, it is emphasized that without the BT method, one cannot draw definite conclusions about the symmetry of the defect from Raman data alone. Of course, in the case of KCl:Li$^+$ the polarized Raman data are clearly consistent with a cubic defect symmetry, but by means of the BT method, one obtains this conclusion in an inductive way.

The observation of an A_{1g} mode of the point group O_h is in disagreement with the interpretation of the ir-active modes. In Ref. 4, a local C_{3v} symmetry was assumed that would split up the ir-active T_{1u} transition into an A_1 and E part. This splitting is not observed at all in Raman scattering. Moreover, a mode of the Li$^+$ in an off-center well would be expected to possess a BT clearly different from that of $O_h{:}A_{1g}$. For the $C_{3v}{:}A_1$ mode, the s IP is different from zero, and for the $C_{3v}{:}E$ modes, the ratio r/q equals $-\frac{1}{2}$, which is, in size and sign, far from the observed value. Therefore, the 43-cm^{-1} centroid observed in Raman belongs as a whole to the totally symmetric representation of the full cubic point group O_h.

This Raman result, together with the fact that isotope substitution from ^{7}Li$^+$ to ^{6}Li$^+$ only results in a small and negative isotope shift[4,8] of the Raman and ir modes, forces one to conclude that the motion of the Li$^+$ ion itself hardly participates in this resonance. We consider the Raman resonance as essentially being due to the collective motion of the surrounding chlorine ions. As such, it is considered to be a first-order induced continuum of (perturbed) lattice phonons and not an envelope of transitions between a ground- and an excited-state tunnel multiplet. This explains the absence in the Raman and ir spectra of any fine structure associated with the tunnel splitting of the ground- or excited-state levels.

B. Comparison to the Raman modes of the $F_A(\mathrm{Li}^+)$ center in KCl

The interpretation given in the preceding subsection is supported by a comparison between the Raman modes of the "naked" Li^+ ion and the $F_A(\mathrm{Li}^+)$ center in KCl. In the $F_A(\mathrm{Li}^+)$ center, the motion of the Li^+ ion can be resonantly probed by exciting the electronic transitions of the associated F center. This was reported by Fritz[14] and by Lüty and co-workers (Refs. 15—17). Three dynamical modes associated with the $F_A(\mathrm{Li}^+)$ center were observed. Two of them lie above or at about the phonon cutoff frequency and exhibit a regular (positive) isotope shift upon $^7\mathrm{Li}^+$ to $^6\mathrm{Li}^+$ substitution. The third mode is centered at $47 \pm 2\ \mathrm{cm}^{-1}$ and shows the negative isotope effect,[17] which was also observed for the naked Li^+ ion in ir and Raman spectroscopy.

We have performed a polarized Raman study of the three $F_A(\mathrm{Li}^+)$ modes, and established that they all belong to the A' representation of the monoclinic C_{1h} symmetry.[18] However, the observed BT of the low-frequency mode corresponds to an A_1 mode of C_{4v}. This means that the off-axis position of the Li^+ ion in $F_A(\mathrm{Li}^+)$ is not reflected in the polarized Raman data of the 47-cm^{-1} mode. Moreover, the orthogonality condition for normal modes implies that the participation of the Li^+-ion motion in the low-frequency resonance of the $F_A(\mathrm{Li}^+)$ center is negligible, since the high-frequency vibrations dominantly involve the motion of the Li^+ ion itself.[18]

The low-frequency resonances of $F_A(\mathrm{Li}^+)$ and Li^+ have a comparable Raman shift and a similar anomalous isotope effect. They both exhibit an observed BT, which does not reflect the off-center position of Li^+. Therefore, it is reasonable that also for the naked Li^+ defect, the impurity ion does not strongly participate in the resonant mode measured in Raman and ir spectroscopy.

C. Nearly degenerate Raman and ir transitions

In the preceding sections, it was shown that the off-center position and the corresponding C_{3v} symmetry of the Li^+ ion is not reflected in the polarized Raman intensities of the 43-cm^{-1} mode. Apparently, the breakdown of cubic symmetry only acts as a small perturbation on the collective motion of the surrounding chlorine ions. However, the displacement of Li^+ away from the inversion center softens the Raman and ir selection rules to such an extent that the same resonant mode is observed with both techniques. In this sense, the off-center position is consistent with a resonant mode, which is both Raman and ir active.

V. THEORETICAL MODEL: A TUNNELING SYSTEM COUPLED TO PERTURBED LATTICE PHONONS

The following type of model Hamiltonian is proposed to study the low-frequency resonances of the Li^+ ion in KCl:

$$\hat{\mathscr{H}} = \hat{H}_{\mathrm{Li}} + \hat{H}_{\mathrm{ph}} + \hat{H}_c \ .$$

$\hat{H}_{\mathrm{Li}}$ is the tunnel Hamiltonian which describes the ground-state multiplet. $\hat{H}_{\mathrm{ph}}$ is the free-phonon Hamiltonian. In general, the phonons are perturbed by the presence of the tunneling ion. As such, $\hat{H}_{\mathrm{ph}}$ already contains information concerning the linewidth and the position of the low-frequency resonant mode. $\hat{H}_c$ describes the interaction between the tunneling and the perturbed lattice phonons. At this point, it is worth noting the recent success of models which include phonon-dressing effects in the description of tunneling dipoles. This way, dielectric relaxation measurements on KCl:Li^+ under tunable hydrostatic pressure have been explained.[19,20] The present Raman study encourages such a theoretical approach, although from an entirely different viewpoint.

We are performing calculations on a specific Hamiltonian of the above form. A key question concerns the negative isotope effect of Li^+ in KCl: Can the interaction term $\hat{H}_c$ shift the maximum of the resonant mode towards higher frequencies with increasing ionic mass, i.e., with a smaller value of the tunnel splitting?

VI. CONCLUDING REMARKS

The BT method was applied to the polarized Raman data of the low-frequency Raman mode of Li^+ in KCl. It follows that an impurity-induced continuum of perturbed lattice modes is observed. From this viewpoint, an extension of the ground-state tunneling model to the vibrational excited state is not appropriate to describe the Raman and ir transitions. A more promising study of the Raman line, its position, and its anomalous isotope effect is now being undertaken within the framework of a model Hamiltonian which describes a tunneling system coupled to a bath of perturbed lattice phonons. It would be interesting to extend the present Raman study to low-frequency resonances of other substitutional defect systems. This way, insight could be gained about the specific effect of the off-center position and of the tunneling behavior on the observability and the isotope shift of Raman- and ir-active modes.

Note added in proof. Fritz Lüty has drawn our attention to a recent interesting paper by H.J.L. Sangster and A. M. Stoneham [Phys. Rev. B **26**, 1028 (1982)] which had completely escaped our attention. These authors studied the ir resonance of Li^+ in KCl on the basis of a direct calculation of the vibrational density of states of an imperfect finite crystal cluster. They too came to the conclusion that the Li^+ ion is not strongly involved in the low-frequency mode in KCl:Li^+ and that the latter is a resonant vibration of the surrounding ions. An interesting prediction of this calculation is the existence of two high-frequency Li^+ modes which, however, have not been observed either in the ir or in the Raman spectra.

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[1] V. Narayanamurti and R. O. Pohl, Rev. Mod. Phys. **42**, 201 (1970).

[2] A. S. Barker, Jr. and A. J. Sievers, Rev. Mod. Phys. **47**, Suppl. 2, 1 (1975).

[3] M. Gomez, S. P. Bowen, and A. J. Krumhansl, Phys. Rev. **153**, 1009 (1967).

[4] R. D. Kirby, A. E. Hughes, and A. J. Sievers, Phys. Rev. B **2**, 481 (1970).

[5] A. M. Kahan, M. Patterson, and A. J. Sievers, Phys. Rev. B **14**, 5422 (1976).

[6] W. Joosen, J. F. Zhou, E. Goovaerts, and D. Schoemaker, Phys. Rev. B **31**, 6709 (1985).

[7] D. Schoemaker, W. Joosen, Z. F. Zhou, and E. Goovaerts, in Proceedings of the International Conference on Defects in Insulating Crystals, Salt Lake City, 1984, p. 410 (unpublished).

[8] A. Mabud and F. Lüty, in Proceedings of the International Conference on Defects in Insulating Crystals, Salt Lake City, 1984, p. 299 (unpublished).

[9] S. A. Mabud and F. Lüty, Bull. Am. Phys. Soc. **28**, 452 (1983).

[10] J. F. Zhou, E. Goovaerts, and D. Schoemaker, Phys. Rev. B **29**, 5509 (1984).

[11] E. Goovaerts, J. F. Zhou, W. Joosen, and D. Schoemaker, Cryst. Latt. Defects Amorph. Mater. **12**, 317 (1985).

[12] J. F. Zhou, E. Goovaerts, and D. Schoemaker, Phys. Rev. B **29**, 5533 (1984).

[13] W. Joosen, E. Goovaerts, and D. Schoemaker, J. Lumin. **31-32**, 317 (1984); Phys. Rev. B **32**, 6748 (1985).

[14] B. Fritz, in *Proceedings of the First International Conference on Localized Excitations in Solids*, edited by R. F. Wallis (Plenum, New York, 1968), p. 496.

[15] F. Lüty, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968).

[16] D. S. Pan and F. Lüty, in Proceedings of the International Conference on Light Scattering in Solids, Campinas, Brasil, 1975 (unpublished).

[17] A. Mabud and F. Lüty, in Proceedings of the International Conference on Defects in Insulating Crystals, Salt Lake City, 1984, Ref. 7, p. 301.

[18] M. Leblans, W. Joosen, E. Goovaerts, and D. Schoemaker (unpublished).

[19] U. Holland and F. Lüty, Phys. Rev. B **19**, 4298 (1979).

[20] R. Beck, W. Götze, and P. Prelovšek, Phys. Rev. A **20**, 1140 (1979).